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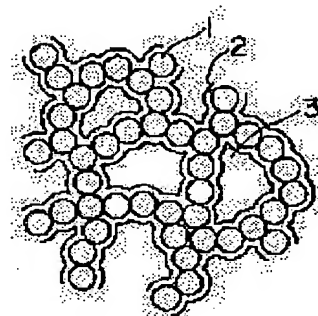
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(54) RECORDING SHEET

(57)Abstract:

PURPOSE: To provide a recording sheet having a colorant receiving layer capable of obtaining a transparent image sheet by ink recording, thermal transfer recording or electrophotographic recording.

CONSTITUTION: In a recording sheet wherein a transparent colorant receiving layer is provided on a transparent support, the colorant receiving layer is one having a three-dimensional reticulated structure with voids of 50-80%. The three-dimensional reticulated structure is formed from fine silica particles 1 with an average primary particle size of 10nm or less and a water soluble resin and the wt. ratio of the fine silica particles 1 and the water-soluble resin 2 is 1.5:1-10:1.



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CLAIMS

[Claim(s)]

[Claim 1] The sheet for record characterized by for this color-material acceptance layer being a layer of the three-dimensional network which has 50 - 80% of voidage in the sheet for record with which it comes to prepare a transparent color-material acceptance layer on a transparence base material, and forming primary [an average of] particle diameter for this three-dimensional network from a silica particle and water soluble resin 10nm or less, and the weight ratio of this silica particle and water soluble resin being in the range of 1.5:1-10:1.

[Claim 2] The sheet for record according to claim 1 with which the pore which forms the opening of this three-dimensional network has the average diameter of 5-30nm.

[Claim 3] This silica particle is 2 1nm to a front face. Sheet for record according to claim 1 which is the silicic anhydride which has the silanol group of 2-3 hits.

[Claim 4] The sheet for record given in ***** claim 1 formed of connection of the aggregated particle which has the particle size this whose three-dimensional network is 10-100nm which the silica particle condensed.

[Claim 5] The sheet for record according to claim 1 this whose water soluble resin is polyvinyl alcohol.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the record sheet recorded using color material. It is related with the record sheet for forming a transparency image sheet by ink record, thermal transfer recording, electrophotography record, etc. especially.

[0002]

[Description of the Prior Art] In recent years, the record approach and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It miniaturizes, there is also no noise and the equipment used in such a record approach in the thermal-ink-transfer-printing record using the ink record using an ink jet or a plotter and melting mold color material, or sublimation mold color material has become a light weight and the thing excellent also in operability and maintainability. Furthermore, the equipment used by such record approach is widely used from colorization being easy recently. Moreover, colorization progresses also in the conventional electrophotography method, and the full color printer and the copying machine have been developed and commercialized with high resolution.

[0003] An ink jet method has three sorts, the approach using the coloring matter solution (water color ink) which roughly divides in physical properties and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low melting point solid wax (wax ink) containing coloring matter, and using it, although various kinds of methods are developed. The mainstream is a type which uses water color ink. Anyway, it is the approach of making an ink record sheet breathe out a liquefied particle drop, and forming an image.

[0004] It is the approach (heat-of-fusion imprint) of dividing a thermal-ink-transfer-printing method greatly, and it having two sorts of methods, and the 1st method carrying out heat impression of the ink of the thermofusion nature by which coating was carried out on the base material from a base material side, making it it carrying out melting to the shape of a pattern which carried out heat impression, making a record sheet-ed imprinting, and obtaining an image. The 2nd method is the approach (heat-of-sublimation imprint) of carrying out heat impression from a base material side like the former, making a sublimation color sublimating to the thermal recording ingredient which consists of the resin and the sublimability color of high softening temperature on a base material in the shape of [which carried out heat impression] a pattern, making a record sheet-ed imprinting, and obtaining an image. An electrophotography method has the approach in use of giving an optical pattern to the electrified photoconduction layer, forming an electrostatic latent image, imprinting to a record sheet-ed after toner development, and carrying out melting fixing of the toner with heat.

[0005] On the other hand, it is necessary to use a transparence sheet, and for the following applications, image formation of many is carried out as mentioned above using the bright film which prepared the color-material acceptance (absorption) layer in the front face, and they create a record sheet. For example, the OHP film whose opportunity used instead of a slide at a meeting etc. is increasing, the film for a back light display whose opportunity used instead of a printing poster or a display board is increasing, the film for mother prints, etc. can be mentioned.

[0006] The bright film by which image formation was carried out by these recording methods requires that color material should have pasted the front face of a record sheet-ed firmly in addition to the hue of the image obtained, saturation, and lightness, and further, in the case of ink jet record, when obtaining a minute image, liquefied ink is absorbed early, and it is required that there is neither ink NIJIMI nor ink *****. In order to solve these troubles, various proposals are made from the former. For example, in ink jet record, use of solubility or the bloating tendency matter is proposed by use of an absorptivity polymer at JP,55-146786,A, and is proposed by the above-mentioned color-material absorption layer at JP,56-80489,A, and many polymer systems (polyvinyl alcohol (PVA), a polyvinyl pyrrolidone (PVP), polyethylene oxide (PEO), carboxymethyl cellulose (CMC)) are proposed. However, the pass-through effect of the water color ink by the hydrophilic radical or dissociative radical of a polymer was used, even when the film was thickened, sufficient ink rate of absorption was not

obtained, and these had inadequate control of a color mixture blot.

[0007] Moreover, the approach of carrying out ink absorption by capillarity is proposed by JP,63-22997,B, JP,63-56876,B, JP,3-21357,B, JP,3-48867,B, JP,57-14091,A, JP,60-61286,A, JP,60-214989,A, JP,61-22983,A, and JP,62-227684,A by using a color-material acceptance layer as porous membrane. Although these are comparatively high about ink absorptivity, since the aperture of porous membrane is too large according to examination of this invention person, it is not suitable for the application as which light is scattered about (diffraction scattering, Mie scattering), and the permeability of light is required since optical transparency is low.

[0008] The method of furthermore using a porosity inorganic pigment for a color-material acceptance layer is proposed by JP,55-144172,A, JP,56-148584,A, JP,56-148585,A, JP,62-273881,A, JP,3-24906,B, JP,60-245588,A, etc. According to examination of this invention person, since the particle size of a pigment is too large, light scattering happens, and these cannot be referred to as that sufficient light transmission nature is shown, either. Moreover, the approach using various kinds of silica particles whose refractive indexes the approach using the non-subtlety particle of a specific refractive index is about 1.45 further at JP,61-53958,B and JP,61-60793,B is proposed by JP,55-51583,A (use of a non-colloid silica), JP,56-148583,A (use of a fines silicic acid), and JP,61-19389,A (use of colloidal silica). Moreover, the approach of using it, making condense the gaseous-phase method silica of 10-30nm of diameters of a primary particle secondarily is proposed by JP,3-56552,B. However, in the color-material acceptance layer which used the porosity inorganic pigment as which only such a refractive index or particle diameter was specified, it became clear that sufficient transparency is not acquired.

[0009] The record sheet with which the color-material acceptance layer which has a detailed hole using a pseudo-boehmite system particle was formed on the other hand is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although these were good about ink absorptivity, since a refractive index was as high as about 1.65, they became clear [that sufficient transparency is not acquired].

[0010]

[Problem(s) to be Solved by the Invention] Especially this invention person came examination in piles variously, in order to obtain the record sheet excellent in the above-mentioned ink absorptivity and transparency. And it became clear to be attained by preparing the color-material acceptance layer formed by making altitude distribute the amount of the binder for distributing this in the condition of having made it decreasing extremely, using the ultrafine particle of a silica on a transparence base material. Moreover, it became clear that the color-material acceptance layer obtained by making altitude distribute the ultrafine particle of a silica in this way had the three-dimensional network which has the opening which consists of very small pore with high voidage. According to such a three-dimensional network, coexistence of the above-mentioned ink absorptivity and transparency is enabled.

[0011] Therefore, this invention aims at offering the sheet for record which has the color-material acceptance layer which can obtain a transparent image sheet by ink record, thermal transfer recording, or electrophotography record. Moreover, transparency of this invention is high and it aims at offering the sheet for record excellent in the hue, saturation, and lightness of the obtained image. Furthermore, this invention absorbs liquefied ink quickly and aims at offering the high sheet for record of transparency suitable for the ink record which can obtain a minute image without ink NIJIMI or ink *****. Moreover, this invention aims at offering the high sheet for record of the transparency which color material pasted the front face of a record sheet-ed firmly in thermal transfer recording, and was excellent in toner adhesion and embossing-proof nature in electrophotography record.

[0012]

[Means for Solving the Problem] In the sheet for record with which it comes to prepare a color-material acceptance layer with the above-mentioned purpose transparent on a transparence base material A color-material acceptance layer is a layer of the three-dimensional network which has 50 - 80% of voidage. And the three-dimensional network can attain with the sheet for record characterized by forming primary [an average of] particle diameter from a silica particle and water soluble resin 10nm or less, and the weight ratio of a silica particle and water soluble resin being in the range of 1.5:1-10:1.

[0013] The desirable mode of the sheet for record of above-mentioned this invention is as follows.

- 1) The above-mentioned sheet for record with which the pore which forms the opening of a three-dimensional network has the average diameter (average pore size) of 5-30nm.
- 2) The above-mentioned sheet for record with which the pore which forms the opening of a three-dimensional network has the pore capacity of 0.5 - 0.9 ml/g.
- 3) The above-mentioned sheet for record whose silica particle is a silicic anhydride.
- 4) A silica particle is 2 1nm to a front face. The above-mentioned sheet for record which has the silanol group of 2-3 hits.
- 5) The above-mentioned sheet for record with which a three-dimensional network consists of a chain formed of connection of the aggregated particle which has the particle size which is 10-100nm which the silica particle

condensed.

6) The above-mentioned sheet for record whose water soluble resin is polyvinyl alcohol.

7) The above-mentioned sheet for record with which a color-material acceptance layer has the specific surface area of 100–250m² / g.

8) The above-mentioned sheet for record with which a color-material acceptance layer has 70% or more of light transmission.

9) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10–50 micrometers.

10) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1–10 micrometers.

[0014] As mentioned above, in the case of water color ink, there are an approach of preparing the absorptivity polymer which has a hydrophilic radical and a dissociative polar group in a color-material acceptance layer, and the approach of making a color-material acceptance layer a vesicular structure as an ink absorber style in ink record from the former. Although excelled in the point with few [ink absorptivity is high and] color mixture blots, since it is porosity and light transmission nature decreases according to light scattering, the direction of the vesicular structure by capillarity is not suitable for the OHP film, the back light display, and the film for mother prints which are used with a transparency mold. In order to raise this light transmission nature and to consider as the structure where voidage is high, moreover, the specific silica of this invention which is the ultrafine particle of a very small particle size which has a refractive index before and behind 1.5 is distributed in dispersion liquid with a small amount of binder resin, and by carrying out spreading desiccation, the color-material acceptance layer in which the three-dimensional network which consists of an aggregated particle of this ultrafine particle was formed can be prepared on a transparency base material, and, thereby, can be attained.

[0015] That is, the sheet for record of this invention has the basic configuration which consists of a transparency base material and a transparent color-material acceptance layer formed on the base material. The color-material acceptance layer of this invention is a layer of the three-dimensional network which has 50 – 80% of voidage, and a three-dimensional network can be acquired, when the weight ratio of a silica particle and water soluble resin uses a silica particle and water soluble resin 10nm or less in 1.5:1–10:1 and primary [an average of] particle diameter forms.

[0016] The mimetic diagram showing the particulate structure (three-dimensional network) of the silica which forms the color-material acceptance layer of this invention is shown in drawing 1 . Moreover, the scanning electron microscope photograph of the particulate structure of the silica of drawing 2 and a cross section is shown for the scanning electron microscope photograph of the particulate structure of the silica of the color-material acceptance layer front face in drawing 3 . While the aggregated particle 1 to which the silica particle covered with water soluble resin 2 condensed the front face forms in drawing 1 the pore 3 which constitutes an opening, the three-dimensional network which connected mutually and was formed is shown. Moreover, drawing 2 and drawing 3 are the photographs taken by one 100,000 times the scale factor of this through the scanning electron microscope in the particulate structure of the silica seen in the front face and cross section of a color-material acceptance layer. It turns out that the mimetic diagram of drawing 1 and the three-dimensional network which corresponded mostly exist in the front face of a color-material acceptance layer, and the interior.

[0017] And a refractive index is 1.45. the silica particle which forms an aggregated particle 1 — the first [an average of] particle diameter — 10nm or less (preferably 3–10nm) — Using this silica particle and by making it distribute using water soluble resin in the amount of the above-mentioned range Since the three-dimension network structure which makes the aggregated particle of a particle a chain unit is formed and micropore is formed in the gap of this network, voidage is very high and the porosity membrane structure of light transmission nature is acquired. Generally, the surface area per weight (specific surface area) becomes large, and the effect of the particle interaction by the surface characteristic becomes strong as particle diameter becomes small. In the sol liquid which distributed the ultrafine particle to altitude in dispersion liquid for this reason, when particles collide in dispersion liquid, the probability for particles to adhere by a surface electrical property and hydrogen bond becomes high, that is, the so-called flocculation with few points of contact of particles (flocculation condition) arises, it becomes the three-dimensions network structure which this connected further, and wet gel arises. If this is dried and dispersion liquid evaporate, in three-dimensions network (reticulated) structure, a detailed opening will be generated and porosity xerogel will generate. If it interprets in a wide sense, it will be application of the method called sol gel process, and, as for this, formation of the color-material acceptance layer of this invention will also use this. the case where formation of an opening detailed in this three-dimensions network structure is so remarkable that a particle becomes small, and the first [an average of] particle diameter uses a silica particle (and the amount of above-mentioned within the limits — water soluble resin — combining) 10nm or less especially like this invention — 30nm or less of pore size with little light scattering — and transparency porous membrane with large voidage can be formed.

[0018] In particles, for an adhesion and cone reason, the first [an average of] particle diameter can form the structure where voidage is large, as mentioned above by the hydrogen bond according [a silica particle] to a surface silanol group in the case of 10nm or less (preferably 3–10nm). A silica particle is divided roughly into a wet method and dry process according to a manufacturing method. The method of a wet method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately, carrying out flocking settling, and obtaining a water silica is in use. One dry-process silica has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of silicon halide with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [a silica] although these water silicas and an anhydrous silica show the property from which there was the difference of the consistency of a surface silanol group, the existence of a hole, etc., and it differed. This reason is 2–8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly, when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2–3 pieces/nm. Since it is few, it is presumed that it becomes **** flocculation (FUROKYU rate) and voidage becomes high structure.

[0019] As for the above-mentioned three-dimensional network, it is desirable to be formed of connection of the aggregated particle which has the particle size which is 10–100nm which the silica particle condensed, and it is desirable. [of further 20–50nm] Moreover, as for 50–80% of voidage of a three-dimensional network, it is desirable that it is 56–80%, as for the pore which forms the opening, it is desirable to have the average diameter (average pore size) of 5–30nm, and its 10–20nm is especially desirable. The capacity (pore capacity) of pore has desirable 0.5–0.9 ml/g, and further 0.6–0.9 ml/g are desirable. Furthermore, the specific surface area of a color-material acceptance layer has the desirable range of 100–250m² / g, and its 120–200m² / g are especially desirable. Moreover, 70% or more of the light transmission of a color-material acceptance layer is desirable.

[0020] The following ingredient may be used in the range which does not spoil the purpose of this invention other than a silica particle. What has a refractive index in 1.40–1.60 from the point of not reducing transparency, as a particle used is desirable, for example, can mention colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, etc.

[0021] In this invention, in order to make easy formation of the three-dimensions style which is a color-material acceptance layer (film) and to raise the film reinforcement, and in order to prevent the cracking crack of the film at the time of desiccation, water soluble resin is used as a binder with a silica particle. The ratio (PB ratio: weight of the silica particle to the weight 1 of water soluble resin) of this silica particle and water soluble resin has big effect also on membrane structure. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. When 10 is exceeded, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, less than by 1.5, an opening is closed by resin, voidage decreases and ink absorptivity ability falls. For this reason, the range of 1.5–10 is suitable for PB ratio. In order to acquire high-speed ink absorptivity with an ink jet printer, as for especially PB ratio, two or more are desirable [to touch directly by hand like especially an OHP film, it is necessary to obtain sufficient film reinforcement, as for especially PB ratio, five or less are desirable, and], therefore the range of 2–5 is still more suitable for PB ratio.

[0022] For example, when the first [an average of] above particle diameter distributed completely [PB ratio / 2–5] in a water solution an anhydrous silica and water soluble resin 10nm or less and carries out spreading desiccation, The three-dimensional network which makes the aggregated particle of a silica particle a chain unit is formed, average pore is 30nm or less, and voidage is 50% or more and the pore specific volume of 0.5ml/g. Specific surface area can form easily the porous membrane (color-material acceptance layer) of the translucency more than 100m²/g above.

[0023] As an example of water soluble resin, as resin which has hydroxyl as a hydrophilic structural unit polyvinyl alcohol (PVA) and cellulose system resin (methyl cellulose (MC) → Ethyl cellulose (EC), hydroxyethyl cellulose (HEC), A carboxymethyl cellulose (CMC) etc. chitins and starch as resin which has; ether linkage Polyethylene oxide (PEO), Polyacrylamide (PAAM) and a polyvinyl pyrrolidone (PVP) can be mentioned as resin which has; an amide group, and amide association for polypropylene oxide (PPO), a polyethylene glycol (PEG), and polyvinyl ether (PVE). Moreover, the poly allylamine (PAA) which has the polystyrene sulfonate salt which has; sulfone radical for the polyacrylate which has a carboxyl group as a dissociative radical, maleic resin, alginate, and gelatin, the amino group, an imino group, the 3rd amine, and the 4th ammonium salt, polyethyleneimine (PEI), an epoxidation polyamide (EPAm), polyvinyl pyridine, and gelatin can be mentioned. The class of resin combined with a silica particle from a viewpoint of transparency is important, and when it is an anhydrous silica, PVA is [whenever / PVA, especially low saponification / (70–90% whenever / saponification / it is desirable)] suitable in respect of light transmission nature. Although PVA has a hydroxyl group in a structural unit, this hydroxyl group and the silanol group of a silica particle front face form hydrogen bond, and it is considered with making

easy to form the three-dimensional network which makes the aggregated particle of a silica particle a chain unit. It is thought that the color-material acceptance layer of the structure where voidage is high is obtained by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither ink NIJIMI nor ink ***** is possible, but the obtained color-material acceptance layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. This reason is because color material etc. is firmly fixed according to the geometrical anchor effect to which color material and a toner go underwater in the pore of a porous layer, and originate in a three-dimensional network as that result. Moreover, since there are many rates of a non-subtlety particle, there is the description that thermal resistance is high and the embossing-proof nature in electrophotography record is also high.

[0024] In ink jet record, the thickness of a color-material acceptance layer needs to have the absorption capacity which absorbs all drops, and it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink 8nl/mm² By the case, if voidage is 60%, film about 15 micrometers or more is needed. In in ink jet record, the range of 10–50 micrometers is desirable. Since color material or a toner is adsorbed on a front face, in the case of thermal ink transfer printing or an electrophotography method, a thin film is enough, and it is desirable. [of 0.1–10 micrometers]

[0025] A single material is sufficient as the silica particle and water soluble resin which mainly constitute this color-material acceptance layer, respectively, and the mixed stock of two or more materials is sufficient as them. moreover, the color-material acceptance layer may contain acid alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of a silica particle and water soluble resin. Moreover, various kinds of surfactants for the purpose which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, a mordant may be used in order to fix coloring matter in ink record and to raise a water resisting property. Moreover, various kinds of mat agents for the purpose which reduces a surface friction property may be included. Moreover, various kinds of antioxidants for the purpose which controls degradation of color material, and an ultraviolet ray absorbent may be included.

[0026] Moreover, between a color-material acceptance layer and a transparence base material, an adhesive property may be raised or undercoat may be prepared for the purpose of adjusting electric resistance. Furthermore, a color-material acceptance layer may be prepared in both sides, in order to prepare in one side of a transparence base material and to control curl etc. Moreover, an antireflection film may be prepared in order to raise light transmission nature to the opposite side, when preparing a color-material acceptance layer only in one side. For the refractive index (nr) of this antireflection film, the refractive index of a transparence base material is ns. It is desirable that the case of near and its thickness is close to $\lambda/4n$ to $ns^{1/2}$ (however, λ is the wavelength of the OHP lamp to be used).

[0027] The film which can be used as the above-mentioned transparence base material is transparent, and if it is an ingredient which has the property to bear the radiant heat when being used on OHP or a back light display, it can be used. As the ingredient, polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned to cellulose ester, such as polyester; nitrocelluloses, such as polyethylene phthalate, cellulose acetate, and cellulose acetate butylate, and a pan. In these, polyethylene phthalate is desirable. Its thickness of a film is easy to deal with a 50–200-micrometer thing and is desirable although there is especially no limit. Moreover, a base material film may use what performed corona discharge treatment, flame treatment, and UV irradiation processing.

[0028] A color-material acceptance layer can be prepared, for example on a transparence base material as follows. The coating liquid for color-material acceptance stratification the silica particle of 10nm or less of diameters of an average primary particle underwater — adding (an example, 10 – 15 % of the weight) — a high-speed rotation wet colloid mill (an example —) After carrying out distribution for 20 minutes (preferably for 10 – 30 minutes) on condition that high-speed rotation of 10000rpm (preferably 5000 – 20000rpm), using a KUREA mix (M Technique Co., Ltd. make), A polyvinyl alcohol water solution (it is set to PVA of about 1/3 weight of an example and a silica like) can be added, and it can distribute on the still more nearly same conditions as the above, and can obtain by subsequently to 4–5 adjusting pH. Thus, the obtained coating liquid is a homogeneity sol and can obtain the color-material acceptance layer which has the three-dimensional network of this invention by forming this on a transparence base material by the following method of application. That is, the water which is a solvent is evaporated by drying, after applying the coating liquid of the above-mentioned homogeneity sol on a base material. When the spreading film reaches gelation concentration by this evaporation, wet gel is formed, when desiccation advances further, porosity xerogel is formed and the color-material acceptance layer of this invention can be obtained.

[0029] Formation of the above-mentioned color-material acceptance layer can carry out the coating liquid which added the antistatic agent etc. to for example, the above-mentioned coating liquid further by request, and was

obtained spreading and by carrying out stoving on the above-mentioned bright film. Spreading can be performed by the well-known methods of application, such as for example, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine. desiccation — hot air drying equipment — comparatively — low temperature — (— preferably, after drying for 0.5 – 3 minutes by 50 – 90 degree-C(3–8m [/second] wind speed)), it is desirable from the point of the crack prevention at the time of desiccation of a color-material acceptance layer when especially thickness is thick to dry further comparatively at an elevated temperature (preferably 120–180 degrees C for 5 – 20 minutes). Moreover, it is possible by letting between roll nips pass under heating and pressurization after spreading and desiccation (for example, a supercalender) and by gloss calender etc. to raise surface smooth nature, transparency, and paint film reinforcement. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[0030]

[Example]

[0031] [Example 1]

(1) The presentation of the coating liquid for color-material acceptance stratification (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 10 weight section refractive index : 1.45; surface silanol group : 2 – 3-/nm²;))

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500; 3.3 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion exchange water The silica particle of 136.0 weight sections ** is added in the ion exchange water (73.3 weight sections) of **. A high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) is used. After making it distribute for 20 minutes on condition that 10000rpm, the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) was added, it distributed on the further still more nearly same conditions as the above, subsequently to 4–5 pH was adjusted, and the coating liquid for color-material acceptance stratification was obtained.

[0032] (2) After having carried out corona discharge treatment of the polyethylene terephthalate front face where the thickness of 100 micrometers carried out biaxial stretching of the coating liquid of spreading *****, using and applying the air knife coater to the front face and drying for 1 minute at 70 degrees C (5m [/second] wind speed) with hot air drying equipment, it dried for 10 minutes at 150 more degrees C. Thereby, desiccation thickness formed the color-material acceptance layer which is 30 micrometers. This obtained the sheet for record for ink jets. The scanning electron microscope photograph (100000 times) of the front face of the obtained color-material acceptance layer and a cross section is shown in drawing 2 and drawing 3 , respectively. These photographs show that the obtained color-material acceptance layer has a three-dimensional network.

[0033] It sets in the [example 1 of comparison] example 1, and is a dry type silica particle (the sheet for record for ink jets was produced like the example 1 except having used refractive-index 1.45;MOX-80 (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 30nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0034] It sets in the [example 2 of comparison] example 1, and is an alumina particle (the sheet for record for ink jets was produced like the example 1 except having used refractive-index 1.75;Aluminium Oxide C (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 13nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0035] In the [example 3 of comparison] example 1, the sheet for record for ink jets was produced like the example 1 except having changed the presentation of the coating liquid for color-material acceptance stratification into the following presentation.

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 6.65 weight section refractive index : 1.45; surface silanol group : 2–3-piece/nm²;))

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500;6.65 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion-exchange-water 86.7 weight section [0036] About the sheet for record for ink jets obtained above, the ink jet fitness was evaluated by the following measuring methods.

(1) With the ink rate-of-absorption ink jet printer (PIXEL JET; product made from Canon), the contact press of the paper was carried out immediately after solid printing of the red to the sheet for record, yellow, blue, and black (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.

AA: Ink was not imprinted by paper.

CC: Ink was imprinted by paper.

(2) it can set using the same printer as the ink color mixture blot above on the red and yellow which were printed by the sheet for record, blue, and a black solid printing section boundary — it oozed out and judged with extent.

AA: It oozes and was poor.

BB: It oozed and ** was accepted for a while.

CC: It oozed out, and it became in ** and accepted.

(3) The diameter of the dot printed by the sheet for record of black ink was measured under the microscope using the same printer as the diameter above of a dot.

(4) The red and yellow which were printed by the sheet for record, blue, and the black solid printing section were measured with the optical-density plan (product made from X-Rite310 TR;X-Rite) using the same printer as the depth-of-shade above. The result of the above-mentioned evaluation is shown in the following table 1.

[0037]

[Table 1]

Table 1 ————— Ink Ink Dot Color ** Whenever Absorption Color mixture
Diameter Yellow Blue Red Black Rate It spreads. (micrometer)

————— Example 1 AA AA 101 1.50 1.28 1.48 1.69 —————
————— Example 1 of a comparison AA AA 108 1.42 1.21 1.40 Example 2 of 1.66 comparisons AA AA
107 1.46 1.26 1.41 Example 3 of 1.67 comparisons CC BB 122 1.38 1.11 1.40 1.59 —————

[0038] About the sheet for record for ink jets obtained above, the physical property was evaluated by the following measuring methods.

(5) Parallel ray permeability was measured using the parallel ray permeability hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make).

(6) They calculated the average by having measured average pore size, (7) voidage, (8) pore specific volume, and (9) specific surface area using the mercury porosimeter (pore sizer 9320-PC2; Shimadzu Corp. make), and having acquired each distribution.

(10) it asked by observing the secondary particle-size profit **** color-material acceptance layer of a silica particle with a scanning electron microscope. The result of the above-mentioned evaluation is shown in the following table 2.

[0039]

[Table 2]

Table 2 ————— Permeability Pore size Voidage Pore specific volume Specific
surface area Secondary particle size (%) (nm) (% (V/V)) (ml/g) (m2/g) (nm)

————— An example 1 81.3 15 61 0.77 162 40 —————
————— The example 1 of a comparison 62.0 35 43 0.45 83 140 The example 2 of a comparison 40.2 21 51
0.52 103 110 Example 3 of a comparison 68.3 1232 0.38 114 40 —————

[0040] [Example 2]

(1) The presentation of the coating liquid for color-material acceptance stratification (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 1 weight section refractive index : 1.45; surface silanol group : 2 - 3-/nm2;)

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500 0.33 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion exchange water The silica particle of 147.97 weight sections ** is added in the ion exchange water (the great portion of 82.3 weight sections) of **. A high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) is used. After making it distribute for 20 minutes on condition that 10000rpm, the polyvinyl alcohol water solution (what was dissolved in the remainder 65.67 weight section of ion exchange water) was added, it distributed on the further still more nearly same conditions as the above, subsequently to 4-5 pH was adjusted, and the coating liquid for color-material acceptance stratification was obtained.

[0041] (2) Corona discharge treatment of the polyethylene terephthalate front face where the thickness of 100 micrometers carried out biaxial stretching of the coating liquid of spreading ***** was carried out, #12 bar air knife coater was used and applied to the front face, and it dried for 10 minutes at 100 degrees C with hot air drying equipment. Thereby, desiccation thickness formed the color-material acceptance layer which is 0.5 micrometers. This obtained the sheet for record for electrophotography. When the obtained color-material acceptance layer was observed with the scanning electron microscope (100000 times), it was admitted that a color-material acceptance layer had a three-dimensional network.

[0042] It sets in the [example 4 of comparison] example 1, and is a dry type silica particle (the sheet for record

for electrophotography was produced like the example 1 except having used refractive-index 1.45;MOX-80 (product made from Japanese Aerosil.) with a primary [an average of] particle diameter of 30nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0043] It sets in the [example 5 of comparison] example 1, and is an alumina particle (the sheet for record for electrophotography was produced like the example 1 except having used refractive-index 1.75;Aluminium Oxide C (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 13nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0044] Thus, the following approach estimated the property for the obtained film for record for electrophotography.

11) The toner adhesion electrophotography copying machine (VIVACE-120; Fuji Xerox make) copied, the whole surface carried out the Scotch tape friction test of the part (black solid part) of an image about the obtained copy film, the optical density of the toner image before and behind Scotch tape exfoliation was measured with the optical-density plan (X-Rite310TR, product made from X-Rite), and the bottom type estimated toner adhesion.

$$\frac{\text{セロテープ剥離後の光学濃度}}{\text{セロテープ剥離前の光学濃度}} \times 100 \quad (\%)$$

[0045] 12) The same electrophotography copying machine as the embossing-proof nature above copied the image, the concavo-convex nonuniformity (if irregularity becomes large, the fall of smooth nature will be brought about) existence of a film was visually observed about the obtained copy film, and embossing-proof nature was evaluated as follows.

AA: There was no concavo-convex nonuniformity of copy film **.

CC: There is concavo-convex nonuniformity of copy film **, and smooth nature was falling.

[0046] 13) The same electrophotography copying machine as the toner imprint concentration above copied the image, and the optical density of the black solid part of the obtained copy film was measured with the optical-density plan (X-Rite310TR, product made from X-Rite). Moreover, it measured also about the physical property of aforementioned (5) - (10). The above-mentioned measurement result ((5) - (10) and (11) - (13)) is shown in the following table 3.

[0047]

[Table 3]

Table 3 ————— Adhesive property En-proof Imprint Permeability Pore size											
Voidage Pore Ratio table Secondary Boss nature Concentration Specific volume Area Particle size (%) (%) , (nm)											
() [% (V/V) (ml/g) (m2/g) (nm)]			Example 283AA 1.14 87 15 60 0.77								
162 40			Example 4 of a comparison 69 AA 1.11 82 35 43 0.45 83140								
Example of comparison 573 AA 1.12 87 21 51 0.52 103 110			[0048]								

[Effect of the Invention] The sheet for record of this invention is a sheet for transparence record which the minute image which absorbs liquefied ink early in ink record, and has neither an ink blot nor ink ***** was obtained, and color material pasted the front face of a record sheet-ed firmly in thermal transfer recording, and was excellent in toner adhesion and embossing-proof nature in electrophotography record. The sheet for record of this invention has a refractive index near 1.5 from which high transparency is easy to be acquired, dispersion reinforcement distributes the specific silica of the ultrafine particle of a small very small particle size in dispersion liquid with a small amount of binder resin at altitude, it is carrying out spreading desiccation and the color-material acceptance layer in which the three-dimensional network which has the minute pore which consists of an aggregated particle of this ultrafine particle was formed is prepared on a transparence base material. Therefore, this color-material acceptance layer has the high voidage which is the layer of the three-dimensional network which has minute pore. That is, since minute pore is formed of the three-dimensional network formed by connection of the aggregated particle of the silica particle of the refractive index near 1.5, transparency with it is shown. [there is little light scattering and high] Moreover, with high voidage, the adhesive property of color material or a toner improves in the absorptivity of ink, blot prevention, and thermal transfer recording and electrophotography record. From the reason for the above, it can be said that the sheet for record of this invention is a transparent sheet for record suitable for the various record approaches.

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TECHNICAL FIELD

[Industrial Application] This invention relates to the record sheet recorded using color material. It is related with the record sheet for forming a transparency image sheet by ink record, thermal transfer recording, electrophotography record, etc. especially.

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PRIOR ART

[Description of the Prior Art] In recent years, the record approach and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It miniaturizes, there is also no noise and the equipment used in such a record approach in the thermal-ink-transfer-printing record using the ink record using an ink jet or a plotter and melting mold color material, or sublimation mold color material has become a light weight and the thing excellent also in operability and maintainability. Furthermore, the equipment used by such record approach is widely used from colorization being easy recently. Moreover, colorization progresses also in the conventional electrophotography method, and the full color printer and the copying machine have been developed and commercialized with high resolution.

[0003] An ink jet method has three sorts, the approach using the coloring matter solution (water color ink) which roughly divides in physical properties and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low melting point solid wax (wax ink) containing coloring matter, and using it, although various kinds of methods are developed. The mainstream is a type which uses water color ink. Anyway, it is the approach of making an ink record sheet breathe out a liquefied particle drop, and forming an image.

[0004] A thermal-ink-transfer-printing method is divided greatly, and has two sorts of methods, and the 1st method is the approach (heat-of-fusion imprint) of carrying out heat impression of the ink of the thermofusion nature by which coating was carried out on the base material from a base material side, carrying out melting to the shape of a pattern which carried out heat impression, making a record sheet-ed imprinting, and obtaining an image. The 2nd method is the approach (heat-of-sublimation imprint) of carrying out heat impression from a base material side like the former, making a sublimation color sublimating to the thermal recording ingredient which consists of the resin and the sublimability color of high softening temperature on a base material in the shape of [which carried out heat impression] a pattern, making a record sheet-ed imprinting, and obtaining an image. An electrophotography method has the approach in use of giving an optical pattern to the electrified photoconduction layer, forming an electrostatic latent image, imprinting to a record sheet-ed after toner development, and carrying out melting fixing of the toner with heat.

[0005] On the other hand, it is necessary to use a transparence sheet, and for the following applications, image formation of many is carried out as mentioned above using the bright film which prepared the color-material acceptance (absorption) layer in the front face, and they create a record sheet. For example, the OHP film whose opportunity used instead of a slide at a meeting etc. is increasing, the film for a back light display whose opportunity used instead of a printing poster or a display board is increasing, the film for mother prints, etc. can be mentioned.

[0006] The bright film by which image formation was carried out by these recording methods requires that color material should have pasted the front face of a record sheet-ed firmly in addition to the hue of the image obtained, saturation, and lightness, and further, in the case of ink jet record, when obtaining a minute image, liquefied ink is absorbed early, and it is required that there is neither ink NIJIMI nor ink *****. In order to solve these troubles, various proposals are made from the former. For example, in ink jet record, use of solubility or the bloating tendency matter is proposed by use of an absorptivity polymer at JP,55-146786,A, and is proposed by the above-mentioned color-material absorption layer at JP,56-80489,A, and many polymer systems (polyvinyl alcohol (PVA), a polyvinyl pyrrolidone (PVP), polyethylene oxide (PEO), carboxymethyl cellulose (CMC)) are proposed. However, the pass-through effect of the water color ink by the hydrophilic radical or dissociative radical of a polymer was used, even when the film was thickened, sufficient ink rate of absorption was not obtained, and these had inadequate control of a color mixture blot.

[0007] Moreover, the approach of carrying out ink absorption by capillarity is proposed by JP,63-22997,B, JP,63-56876,B, JP,3-21357,B, JP,3-48867,B, JP,57-14091,A, JP,60-61286,A, JP,60-214989,A, JP,61-22983,A, and JP,62-227684,A by using a color-material acceptance layer as porous membrane. Although these are comparatively high about ink absorptivity, since the aperture of porous membrane is too large according to examination of this invention person, it is not suitable for the application as which light is scattered about

(diffraction scattering, Mie scattering), and the permeability of light is required since optical transparency is low.

[0008] The method of furthermore using a porosity inorganic pigment for a color-material acceptance layer is proposed by JP,55-144172,A, JP,56-148584,A, JP,56-148585,A, JP,62-273881,A, JP,3-24906,B, JP,60-245588,A, etc. According to examination of this invention person, since the particle size of a pigment is too large, light scattering happens, and these cannot be referred to as that sufficient light transmission nature is shown, either. Moreover, the approach using various kinds of silica particles whose refractive indexes the approach using the non-subtlety particle of a specific refractive index is about 1.45 further at JP,61-53958,B and JP,61-60793,B is proposed by JP,55-51583,A (use of a non-colloid silica), JP,56-148583,A (use of a fines silicic acid), and JP,61-19389,A (use of colloidal silica). Moreover, the approach of using it, making condense the gaseous-phase method silica of 10-30nm of diameters of a primary particle secondarily is proposed by JP,3-56552,B. However, in the color-material acceptance layer which used the porosity inorganic pigment as which only such a refractive index or particle diameter was specified, it became clear that sufficient transparency is not acquired.

[0009] The record sheet with which the color-material acceptance layer which has a detailed hole using a pseudo-boehmite system particle was formed on the other hand is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although these were good about ink absorptivity, since a refractive index was as high as about 1.65, they became clear [that sufficient transparency is not acquired].

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EFFECT OF THE INVENTION

[Effect of the Invention] The sheet for record of this invention is a sheet for transparence record which the minute image which absorbs liquefied ink early in ink record, and has neither an ink blot nor ink ***** was obtained, and color material pasted the front face of a record sheet-ed firmly in thermal transfer recording, and was excellent in toner adhesion and embossing-proof nature in electrophotography record. The sheet for record of this invention has a refractive index near 1.5 from which high transparency is easy to be acquired, dispersion reinforcement distributes the specific silica of the ultrafine particle of a small very small particle size in dispersion liquid with a small amount of binder resin at altitude, it is carrying out spreading desiccation and the color-material acceptance layer in which the three-dimensional network which has the minute pore which consists of an aggregated particle of this ultrafine particle was formed is prepared on a transparence base material. Therefore, this color-material acceptance layer has the high voidage which is the layer of the three-dimensional network which has minute pore. That is, since minute pore is formed of the three-dimensional network formed by connection of the aggregated particle of the silica particle of the refractive index near 1.5, transparency with it is shown. [there is little light scattering and high] Moreover, with high voidage, the adhesive property of color material or a toner improves in the absorptivity of ink, blot prevention, and thermal transfer recording and electrophotography record. From the reason for the above, it can be said that the sheet for record of this invention is a transparent sheet for record suitable for the various record approaches.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Especially this invention person came examination in piles variously, in order to obtain the record sheet excellent in the above-mentioned ink absorptivity and transparency. And it became clear to be attained by preparing the color-material acceptance layer formed by making altitude distribute the amount of the binder for distributing this in the condition of having made it decreasing extremely, using the ultrafine particle of a silica on a transparence base material. Moreover, it became clear that the color-material acceptance layer obtained by making altitude distribute the ultrafine particle of a silica in this way had the three-dimensional network which has the opening which consists of very small pore with high voidage. According to such a three-dimensional network, coexistence of the above-mentioned ink absorptivity and transparency is enabled.

[0011] Therefore, this invention aims at offering the sheet for record which has the color-material acceptance layer which can obtain a transparent image sheet by ink record, thermal transfer recording, or electrophotography record. Moreover, transparency of this invention is high and it aims at offering the sheet for record excellent in the hue, saturation, and lightness of the obtained image. Furthermore, this invention absorbs liquefied ink quickly and aims at offering the high sheet for record of transparency suitable for the ink record which can obtain a minute image without ink NIJIMI or ink *****. Moreover, this invention aims at offering the high sheet for record of the transparency which color material pasted the front face of a record sheet-ed firmly in thermal transfer recording, and was excellent in toner adhesion and embossing-proof nature in electrophotography record.

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MEANS

[Means for Solving the Problem] In the sheet for record with which it comes to prepare a color-material acceptance layer with the above-mentioned purpose transparent on a transparence base material A color-material acceptance layer is a layer of the three-dimensional network which has 50 – 80% of voidage. And the three-dimensional network can attain with the sheet for record characterized by forming primary [an average of] particle diameter from a silica particle and water soluble resin 10nm or less, and the weight ratio of a silica particle and water soluble resin being in the range of 1.5:1–10:1.

[0013] The desirable mode of the sheet for record of above-mentioned this invention is as follows.

- 1) The above-mentioned sheet for record with which the pore which forms the opening of a three-dimensional network has the average diameter (average pore size) of 5–30nm.
- 2) The above-mentioned sheet for record with which the pore which forms the opening of a three-dimensional network has the pore capacity of 0.5 – 0.9 ml/g.
- 3) The above-mentioned sheet for record whose silica particle is a silicic anhydride.
- 4) A silica particle is 2 1nm to a front face. The above-mentioned sheet for record which has the silanol group of 2–3 hits.
- 5) The above-mentioned sheet for record with which a three-dimensional network consists of a chain formed of connection of the aggregated particle which has the particle size which is 10–100nm which the silica particle condensed.
- 6) The above-mentioned sheet for record whose water soluble resin is polyvinyl alcohol.
- 7) The above-mentioned sheet for record with which a color-material acceptance layer has the specific surface area of 100–250m² / g.
- 8) The above-mentioned sheet for record with which a color-material acceptance layer has 70% or more of light transmission.
- 9) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10–50 micrometers.
- 10) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1–10 micrometers.

[0014] As mentioned above, in the case of water color ink, there are an approach of preparing the absorptivity polymer which has a hydrophilic radical and a dissociative polar group in a color-material acceptance layer, and the approach of making a color-material acceptance layer a vesicular structure as an ink absorber style in ink record from the former. Although excelled in the point with few [ink absorptivity is high and] color mixture blots, since it is porosity and light transmission nature decreases according to light scattering, the direction of the vesicular structure by capillarity is not suitable for the OHP film, the back light display, and the film for mother prints which are used with a transparency mold. In order to raise this light transmission nature and to consider as the structure where voidage is high, moreover, the specific silica of this invention which is the ultrafine particle of a very small particle size which has a refractive index before and behind 1.5 is distributed in dispersion liquid with a small amount of binder resin, and by carrying out spreading desiccation, the color-material acceptance layer in which the three-dimensional network which consists of an aggregated particle of this ultrafine particle was formed can be prepared on a transparence base material, and, thereby, can be attained.

[0015] That is, the sheet for record of this invention has the basic configuration which consists of a transparence base material and a transparent color-material acceptance layer formed on the base material. The color-material acceptance layer of this invention is a layer of the three-dimensional network which has 50 – 80% of voidage, and a three-dimensional network can be acquired, when the weight ratio of a silica particle and water soluble resin uses a silica particle and water soluble resin 10nm or less in 1.5:1–10:1 and primary [an average of] particle diameter forms.

[0016] The mimetic diagram showing the particulate structure (three-dimensional network) of the silica which forms the color-material acceptance layer of this invention is shown in drawing 1 . Moreover, the scanning electron microscope photograph of the particulate structure of the silica of drawing 2 and a cross section is

shown for the scanning electron microscope photograph of the particulate structure of the silica of the color-material acceptance layer front face in drawing 3. While the aggregated particle 1 to which the silica particle covered with water soluble resin 2 condensed the front face forms in drawing 1 the pore 3 which constitutes an opening, the three-dimensional network which connected mutually and was formed is shown. Moreover, drawing 2 and drawing 3 are the photographs taken by one 100,000 times the scale factor of this through the scanning electron microscope in the particulate structure of the silica seen in the front face and cross section of a color-material acceptance layer. It turns out that the mimetic diagram of drawing 1 and the three-dimensional network which corresponded mostly exist in the front face of a color-material acceptance layer, and the interior.

[0017] And a refractive index is 1.45. the silica particle which forms an aggregated particle 1 — the first [an average of] particle diameter — 10nm or less (preferably 3–10nm) — Using this silica particle and by making it distribute using water soluble resin in the amount of the above-mentioned range Since the three-dimension network structure which makes the aggregated particle of a particle a chain unit is formed and micropore is formed in the gap of this network, voidage is very high and the porosity membrane structure of light transmission nature is acquired. Generally, the surface area per weight (specific surface area) becomes large, and the effect of the particle interaction by the surface characteristic becomes strong as particle diameter becomes small. In the sol liquid which distributed the ultrafine particle to altitude in dispersion liquid for this reason, when particles collide in dispersion liquid, the probability for particles to adhere by a surface electrical property and hydrogen bond becomes high, that is, the so-called flocculation with few points of contact of particles (flocculation condition) arises, it becomes the three-dimensions network structure which this connected further, and wet gel arises. If this is dried and dispersion liquid evaporate, in three-dimensions network (reticulated) structure, a detailed opening will be generated and porosity xerogel will generate. If it interprets in a wide sense, it will be application of the method called sol gel process, and, as for this, formation of the color-material acceptance layer of this invention will also use this. the case where formation of an opening detailed in this three-dimensions network structure is so remarkable that a particle becomes small, and the first [an average of] particle diameter uses a silica particle (and the amount of above-mentioned within the limits — water soluble resin — combining) 10nm or less especially like this invention — 30nm or less of pore size with little light scattering — and transparence porous membrane with large voidage can be formed.

[0018] In particles, for an adhesion and cone reason, the first [an average of] particle diameter can form the structure where voidage is large, as mentioned above by the hydrogen bond according [a silica particle] to a surface silanol group in the case of 10nm or less (preferably 3–10nm). A silica particle is divided roughly into a wet method and dry process according to a manufacturing method. The method of a wet method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately, carrying out flocking settling, and obtaining a water silica is in use. One dry-process silica has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of silicon halide with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [a silica] although these water silicas and an anhydrous silica show the property from which there was the difference of the consistency of a surface silanol group, the existence of a hole, etc., and it differed. This reason is 2 5–8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly, when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2 2–3 pieces/nm. Since it is few, it is presumed that it becomes **** flocculation (FUKOKYU rate) and voidage becomes high structure.

[0019] As for the above-mentioned three-dimensional network, it is desirable to be formed of connection of the aggregated particle which has the particle size which is 10–100nm which the silica particle condensed, and it is desirable. [of further 20–50nm] Moreover, as for 50 – 80% of voidage of a three-dimensional network, it is desirable that it is 56 – 80%, as for the pore which forms the opening, it is desirable to have the average diameter (average pore size) of 5–30nm, and its 10–20nm is especially desirable. The capacity (pore capacity) of pore has desirable 0.5 – 0.9 ml/g, and further 0.6 – its 0.9 ml/g are desirable. Furthermore, the specific surface area of a color-material acceptance layer has the desirable range of 100–250m² / g, and its 120–200m² / g are especially desirable. Moreover, 70% or more of the light transmission of a color-material acceptance layer is desirable.

[0020] The following ingredient may be used in the range which does not spoil the purpose of this invention other than a silica particle. What has a refractive index in 1.40–1.60 from the point of not reducing transparency, as a particle used is desirable, for example, can mention colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, etc.

[0021] In this invention, in order to make easy formation of the three-dimensions style which is a color-material acceptance layer (film) and to raise the film reinforcement, and in order to prevent the cracking crack of the film at the time of desiccation, water soluble resin is used as a binder with a silica particle. The ratio (PB ratio:

weight of the silica particle to the weight 1 of water soluble resin) of this silica particle and water soluble resin has big effect also on membrane structure. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. When 10 is exceeded, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, less than by 1.5, an opening is closed by resin, voidage decreases and ink absorptivity ability falls. For this reason, the range of 1.5–10 is suitable for PB ratio. In order to acquire high-speed ink absorptivity with an ink jet printer, as for especially PB ratio, two or more are desirable [to touch directly by hand like especially an OHP film, it is necessary to obtain sufficient film reinforcement, as for especially PB ratio, five or less are desirable, and], therefore the range of 2–5 is still more suitable for PB ratio. [0022] For example, when the first [an average of] above particle diameter distributed completely [PB ratio / 2–5] in a water solution an anhydrous silica and water soluble resin 10nm or less and carries out spreading desiccation, The three-dimensional network which makes the aggregated particle of a silica particle a chain unit is formed, average pore is 30nm or less, and voidage is 50% or more and the pore specific volume of 0.5ml/g. Specific surface area can form easily the porous membrane (color-material acceptance layer) of the translucency more than 100m²/g above.

[0023] As an example of water soluble resin, as resin which has hydroxyl as a hydrophilic structural unit polyvinyl alcohol (PVA) and cellulose system resin (methyl cellulose (MC) —) Ethyl cellulose (EC), hydroxyethyl cellulose (HEC), A carboxymethyl cellulose (CMC) etc. chitins and starch as resin which has; ether linkage Polyethylene oxide (PEO), Polyacrylamide (PAAM) and a polyvinyl pyrrolidone (PVP) can be mentioned as resin which has; an amide group, and amide association for polypropylene oxide (PPO), a polyethylene glycol (PEG), and polyvinyl ether (PVE). Moreover, the poly allylamine (PAA) which has the polystyrene sulfonate salt which has; sulfone radical for the polyacrylate which has a carboxyl group as a dissociative radical, maleic resin, alginate, and gelatin, the amino group, an imino group, the 3rd amine, and the 4th ammonium salt, polyethyleneimine (PEI), an epoxidation polyamide (EPAM), polyvinyl pyridine, and gelatin can be mentioned. The class of resin combined with a silica particle from a viewpoint of transparency is important, and when it is an anhydrous silica, PVA is [whenever / PVA, especially low saponification / (70 – 90% whenever / saponification / it is desirable)] suitable in respect of light transmission nature. Although PVA has a hydroxyl group in a structural unit, this hydroxyl group and the silanol group of a silica particle front face form hydrogen bond, and it is considered with making easy to form the three-dimensional network which makes the aggregated particle of a silica particle a chain unit. It is thought that the color-material acceptance layer of the structure where voidage is high is obtained by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither ink NIIJMI nor ink ***** is possible, but the obtained color-material acceptance layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. This reason is because color material etc. is firmly fixed according to the geometrical anchor effect to which color material and a toner go underwater in the pore of a porous layer, and originate in a three-dimensional network as that result. Moreover, since there are many rates of a non-subtlety particle, there is the description that thermal resistance is high and the embossing-proof nature in electrophotography record is also high.

[0024] In ink jet record, the thickness of a color-material acceptance layer needs to have the absorption capacity which absorbs all drops, and it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink 8nl/mm² By the case, if voidage is 60%, film about 15 micrometers or more is needed. In in ink jet record, the range of 10–50 micrometers is desirable. Since color material or a toner is adsorbed on a front face, in the case of thermal ink transfer printing or an electrophotography method, a thin film is enough, and it is desirable. [of 0.1–10 micrometers]

[0025] A single material is sufficient as the silica particle and water soluble resin which mainly constitute this color-material acceptance layer, respectively, and the mixed stock of two or more materials is sufficient as them. moreover, the color-material acceptance layer may contain acid alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of a silica particle and water soluble resin. Moreover, various kinds of surfactants for the purpose which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, a mordant may be used in order to fix coloring matter in ink record and to raise a water resisting property. Moreover, various kinds of mat agents for the purpose which reduces a surface friction property may be included. Moreover, various kinds of antioxidants for the purpose which controls degradation of color material, and an ultraviolet ray absorbent may be included.

[0026] Moreover, between a color-material acceptance layer and a transparence base material, an adhesive property may be raised or undercoat may be prepared for the purpose of adjusting electric resistance. Furthermore, a color-material acceptance layer may be prepared in both sides, in order to prepare in one side of a transparence base material and to control curl etc. Moreover, an antireflection film may be prepared in order to raise light transmission nature to the opposite side, when preparing a color-material acceptance layer only in

one side. For the refractive index (n_r) of this antireflection film, the refractive index of a transparency base material is n_s . It is desirable that the case of near and its thickness is close to $\lambda/4n$ to $n_s/2$ (however, λ is the wavelength of the OHP lamp to be used).

[0027] The film which can be used as the above-mentioned transparency base material is transparent, and if it is an ingredient which has the property to bear the radiant heat when being used on OHP or a back light display, it can be used. As the ingredient, polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned to cellulose ester, such as polyester; nitrocelluloses, such as polyethylene phthalate, cellulose acetate, and cellulose acetate butylate, and a pan. In these, polyethylene phthalate is desirable. Its thickness of a film is easy to deal with a 50–200-micrometer thing and is desirable although there is especially no limit. Moreover, a base material film may use what performed corona discharge treatment, flame treatment, and UV irradiation processing.

[0028] A color-material acceptance layer can be prepared, for example on a transparency base material as follows. The coating liquid for color-material acceptance stratification the silica particle of 10nm or less of diameters of an average primary particle underwater — adding (an example, 10 – 15 % of the weight) — a high-speed rotation wet colloid mill (an example —) After carrying out distribution for 20 minutes (preferably for 10 – 30 minutes) on condition that high-speed rotation of 10000rpm (preferably 5000 – 20000rpm), using a KUREA mix (M Technique Co., Ltd. make), A polyvinyl alcohol water solution (it is set to PVA of about 1/3 weight of an example and a silica like) can be added, and it can distribute on the still more nearly same conditions as the above, and can obtain by subsequently to 4–5 adjusting pH. Thus, the obtained coating liquid is a homogeneity sol and can obtain the color-material acceptance layer which has the three-dimensional network of this invention by forming this on a transparency base material by the following method of application. That is, the water which is a solvent is evaporated by drying, after applying the coating liquid of the above-mentioned homogeneity sol on a base material. When the spreading film reaches gelation concentration by this evaporation, wet gel is formed, when desiccation advances further, porosity xerogel is formed and the color-material acceptance layer of this invention can be obtained.

[0029] Formation of the above-mentioned color-material acceptance layer can carry out the coating liquid which added the antistatic agent etc. to for example, the above-mentioned coating liquid further by request, and was obtained spreading and by carrying out stoving on the above-mentioned bright film. Spreading can be performed by the well-known methods of application, such as for example, the Ayr doctor coating machine, a bread coating machine, a rod coating machine, a knife coating machine, a squeeze coating machine, a reverse roll coater, and a bar coating machine. desiccation — hot air drying equipment — comparatively — low temperature — (— preferably, after drying for 0.5 – 3 minutes by 50 – 90 degree-C(3–8m [/second] wind speed)), it is desirable from the point of the crack prevention at the time of desiccation of a color-material acceptance layer when especially thickness is thick to dry further comparatively at an elevated temperature (preferably 120–180 degrees C for 5 – 20 minutes). Moreover, it is possible by letting between roll nips pass under heating and pressurization after spreading and desiccation (for example, a supercalender) and by gloss calender etc. to raise surface smooth nature, transparency, and paint film reinforcement. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[Translation done.]

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EXAMPLE

[Example]

[0031] [Example 1]

(1) The presentation of the coating liquid for color-material acceptance stratification (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 10 weight section refractive index : 1.45; surface silanol group : 2 - 3-/nm²;))

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500; 3.3 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion exchange water The silica particle of 136.0 weight sections ** is added in the ion exchange water (73.3 weight sections) of **. A high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) is used. After making it distribute for 20 minutes on condition that 10000rpm, the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) was added, it distributed on the further still more nearly same conditions as the above, subsequently to 4-5 pH was adjusted, and the coating liquid for color-material acceptance stratification was obtained.

[0032] (2) After having carried out corona discharge treatment of the polyethylene terephthalate front face where the thickness of 100 micrometers carried out biaxial stretching of the coating liquid of spreading *****, using and applying the air knife coater to the front face and drying for 1 minute at 70 degrees C (5m [/second] wind speed) with hot air drying equipment, it dried for 10 minutes at 150 more degrees C. Thereby, desiccation thickness formed the color-material acceptance layer which is 30 micrometers. This obtained the sheet for record for ink jets. The scanning electron microscope photograph (100000 times) of the front face of the obtained color-material acceptance layer and a cross section is shown in drawing 2 and drawing 3 , respectively. These photographs show that the obtained color-material acceptance layer has a three-dimensional network.

[0033] It sets in the [example 1 of comparison] example 1, and is a dry type silica particle (the sheet for record for ink jets was produced like the example 1 except having used refractive-index 1.45;MOX-80 (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 30nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0034] It sets in the [example 2 of comparison] example 1, and is an alumina particle (the sheet for record for ink jets was produced like the example 1 except having used refractive-index 1.75;Aluminium Oxide C (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 13nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0035] In the [example 3 of comparison] example 1, the sheet for record for ink jets was produced like the example 1 except having changed the presentation of the coating liquid for color-material acceptance stratification into the following presentation.

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 6.65 weight section refractive index : 1.45; surface silanol group : 2-3-piece/nm²;))

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500;6.65 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion exchange water The 86.7 weight sections [0036] About the sheet for record for ink jets obtained above, the ink jet fitness was evaluated by the following measuring methods.

(1) With the ink rate-of-absorption ink jet printer (PIXEL JET; product made from Canon), the contact press of the paper was carried out immediately after solid printing of the red to the sheet for record, yellow, blue, and black (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.

AA: Ink was not imprinted by paper.

CC: Ink was imprinted by paper.

(2) it can set using the same printer as the ink color mixture blot above on the red and yellow which were

printed by the sheet for record, blue, and a black solid printing section boundary — it oozed out and judged with extent.

AA: It oozes and was poor.

BB: It oozed and ** was accepted for a while.

CC: It oozed out, and it became in ** and accepted.

(3) The diameter of the dot printed by the sheet for record of black ink was measured under the microscope using the same printer as the diameter above of a dot.

(4) The red and yellow which were printed by the sheet for record, blue, and the black solid printing section were measured with the optical-density plan (product made from X-Rite310 TR;X-Rite) using the same printer as the depth-of-shade above. The result of the above-mentioned evaluation is shown in the following table 1.

[0037]

[Table 1]

Table 1 ————— Ink Ink Dot Color ** Whenever Absorption Color mixture
Diameter Yellow Blue Red Black Rate It spreads. (micrometer)

————— Example 1 AA AA 101 1.50 1.28 1.48 1.69 —————
————— Example 1 of a comparison AA AA 108 1.42 1.21 1.40 Example 2 of 1.66 comparisons AA AA
107 1.46 1.26 1.41 Example 3 of 1.67 comparisons CC BB 122 1.38 1.11 1.40 1.59 —————

[0038] About the sheet for record for ink jets obtained above, the physical property was evaluated by the following measuring methods.

(5) Parallel ray permeability was measured using the parallel ray permeability hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make).

(6) They calculated the average by having measured average pore size, (7) voidage, (8) pore specific volume, and (9) specific surface area using the mercury porosimeter (pore sizer 9320-PC2; Shimadzu Corp. make), and having acquired each distribution.

(10) it asked by observing the secondary particle-size profit **** color-material acceptance layer of a silica particle with a scanning electron microscope. The result of the above-mentioned evaluation is shown in the following table 2.

[0039]

[Table 2]

Table 2 ————— Permeability Pore size Voidage Pore specific volume Specific
surface area Secondary particle size (%) (nm) (% (V/V)) (ml/g) (m2/g) (nm)

————— An example 1 81.3 15 61 0.77 162 40 —————
————— The example 1 of a comparison 62.0 35 43 0.45 83 140 The example 2 of a comparison 40.2 21 51
0.52 103 110 Example 3 of a comparison 68.3 1232 0.38 114 40 —————

[0040] [Example 2]

(1) The presentation of the coating liquid for color-material acceptance stratification (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

** Dry type silica particle (primary [an average of] particle diameter: 7nm; 1 weight section refractive index : 1.45; surface silanol group : 2 - 3-/nm2;)

Aerosil A300 (product made from Japanese Aerosil)

** Polyvinyl alcohol (it is the 88%; polymerization-degree 3500 0.33 weight section whenever [saponification] PVA235 (Kuraray Co., Ltd. make))

** Ion exchange water The silica particle of 147.97 weight sections ** is added in the ion exchange water (the great portion of 82.3 weight sections) of **. A high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) is used. After making it distribute for 20 minutes on condition that 10000rpm, the polyvinyl alcohol water solution (what was dissolved in the remainder 65.67 weight section of ion exchange water) was added, it distributed on the further still more nearly same conditions as the above, subsequently to 4-5 pH was adjusted, and the coating liquid for color-material acceptance stratification was obtained.

[0041] (2) Corona discharge treatment of the polyethylene terephthalate front face where the thickness of 100 micrometers carried out biaxial stretching of the coating liquid of spreading ***** was carried out, #12 bar air knife coater was used and applied to the front face, and it dried for 10 minutes at 100 degrees C with hot air drying equipment. Thereby, desiccation thickness formed the color-material acceptance layer which is 0.5 micrometers. This obtained the sheet for record for electrophotography. When the obtained color-material acceptance layer was observed with the scanning electron microscope (100000 times), it was admitted that a color-material acceptance layer had a three-dimensional network.

[0042] It sets in the [example 4 of comparison] example 1, and is a dry type silica particle (the sheet for record for electrophotography was produced like the example 1 except having used refractive-index 1.45;MOX-80 (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 30nm instead of a

dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0043] It sets in the [example 5 of comparison] example 1, and is an alumina particle (the sheet for record for electrophotography was produced like the example 1 except having used refractive-index 1.75;Aluminium Oxide C (product made from Japanese Aerosil).) with a primary [an average of] particle diameter of 13nm instead of a dry type silica particle with a primary [an average of] particle diameter of 7nm.

[0044] Thus, the following approach estimated the property for the obtained film for record for electrophotography.

11) The toner adhesion electrophotography copying machine (VIVACE-120; Fuji Xerox make) copied, the whole surface carried out the Scotch tape friction test of the part (black solid part) of an image about the obtained copy film, the optical density of the toner image before and behind Scotch tape exfoliation was measured with the optical-density plan (X-Rite310TR, product made from X-Rite), and the bottom type estimated toner adhesion.

$$\frac{\text{セロテープ剥離後の光学濃度}}{\text{セロテープ剥離前の光学濃度}} \times 100 \quad (\%)$$

[0045] 12) The same electrophotography copying machine as the embossing-proof nature above copied the image, the concavo-convex nonuniformity (if irregularity becomes large, the fall of smooth nature will be brought about) existence of a film was visually observed about the obtained copy film, and embossing-proof nature was evaluated as follows.

AA: There was no concavo-convex nonuniformity of copy film **.

CC: There is concavo-convex nonuniformity of copy film **, and smooth nature was falling.

[0046] 13) The same electrophotography copying machine as the toner imprint concentration above copied the image, and the optical density of the black solid part of the obtained copy film was measured with the optical-density plan (X-Rite310TR, product made from X-Rite). Moreover, it measured also about the physical property of aforementioned (5) - (10). The above-mentioned measurement result ((5) - (10) and (11) - (13)) is shown in the following table 3.

[0047]

[Table 3]

Table 3										Adhesive property En-proof Imprint Permeability Pore size									
Voidage Pore Ratio table Secondary Boss nature Concentration Specific volume Area Particle size (%) (%) , (nm)										Example 283AA 1.14 87 15 60 0.77									
() [%(V/V) (ml/g) (m2/g) (nm)]										Example 4 of a comparison 69 AA 1.11 82 35 43 0.45 83140									
162	40																		
Example of comparison 573 AA 1.12 87 21 51 0.52 103 110																			

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram showing an example of the particulate structure of the silica which forms the color-material acceptance layer of this invention.

[Drawing 2] It is the scanning electron microscope photograph of an example of the particulate structure of the silica which forms the front face of the color-material acceptance layer of this invention.

[Drawing 3] It is the scanning electron microscope photograph of an example of the particulate structure of the silica which forms the cross section of the color-material acceptance layer of this invention.

[Description of Notations]

- 1 Aggregated Particle Which Silica Particle Condensed
- 2 Water Soluble Resin
- 3 Pore

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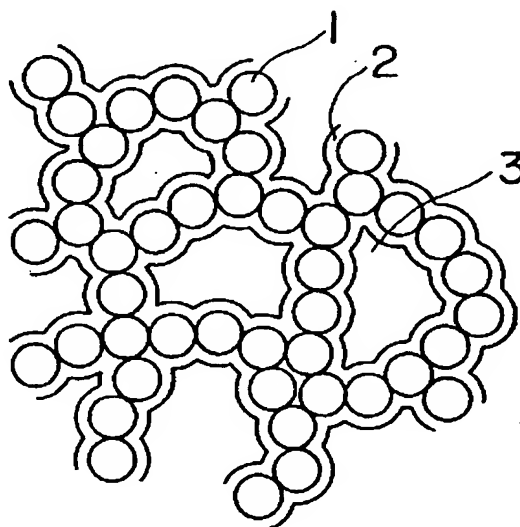
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(54)【発明の名称】 記録用シート

(57)【要約】

【目的】 インク記録、熱転写記録又は電子写真記録により透明な画像シートを得ることができる色材受容層を有する記録用シートを提供する。

【構成】 透明支持体上に、透明な色材受容層が設けられてなる記録用シートにおいて、該色材受容層が、空隙率50～80%を有する三次元網目構造の層であり、そして該三次元網目構造が、平均1次粒子径が10nm以下のシリカ微粒子と水溶性樹脂とから形成されており、且つ該シリカ微粒子と水溶性樹脂の重量比が1.5:1～10:1の範囲にあることを特徴とする記録用シート。



【特許請求の範囲】

【請求項 1】 透明支持体上に、透明な色材受容層が設けられてなる記録用シートにおいて、該色材受容層が、空隙率 50～80%を有する三次元網目構造の層であり、そして該三次元網目構造が、平均 1 次粒子径が 10 nm 以下のシリカ微粒子と水溶性樹脂とから形成されており、且つ該シリカ微粒子と水溶性樹脂の重量比が 1.5:1～10:1 の範囲にあることを特徴とする記録用シート。

【請求項 2】 該三次元網目構造の空隙を形成する細孔が、5～30 nm の平均直径を有する請求項 1 に記載の記録用シート。

【請求項 3】 該シリカ微粒子が、表面に 1 nm² 当たり 2～3 個のシラノール基を有する無水珪酸である請求項 1 に記載の記録用シート。

【請求項 4】 該三次元網目構造が、シリカ微粒子が凝集した 10～100 nm の粒径を有する二次粒子の連結により形成されている請求項 1 に記載の記録用シート。

【請求項 5】 該水溶性樹脂が、ポリビニルアルコールである請求項 1 に記載の記録用シート。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は色材を用いて記録する記録シートに関するものである。特に、インク記録、熱転写記録及び電子写真記録等により透明画像シートを形成するための記録シートに関する。

【0002】

【従来の技術】 近年、情報産業の急速な発展に伴い、種々の情報処理システムが開発され、また、それぞれの情報システムに適した記録方法及び装置も開発され、採用されている。このような記録方法の中で、インクジェットあるいはプロッターを用いたインク記録、及び溶融型色材あるいは昇華型色材を用いた感熱転写記録においては、使用する装置が、軽量かつコンパクト化され、騒音もなく、操作性、保守性にも優れたものとなっている。さらに、このような記録方法で使用する装置はカラー化も容易であることから、最近広く使用されている。また、従来の電子写真方式においてもカラー化が進み高解像度でフルカラーのプリンター、複写機が開発され商品化されてきている。

【0003】 インクジェット方式は各種の方式が開発されているが、物性的には大きく分けて水溶性色素を含む色素溶液（水性インク）を用いる方法、及び油性色素を含む色素溶液（油性インク）を用いる方法、そして色素を含有した低融点固形ワックス（ワックスインク）を熱溶融させて用いる方法の三種がある。主流は水性インクを使用するタイプである。何れにしてもインク記録シートに液状の微粒滴を吐出させて画像を形成する方法である。

【0004】 感熱転写方式は、大きくわけて二種の方式があり、第 1 の方式は支持体上に塗工された熱溶融性のインクを支持体側から熱印加し熱印加したパターン状に溶融させて被記録シートに転写させて画像を得る方法

（溶融熱転写）であり、第 2 の方式は支持体上に高軟化点の樹脂と昇華性染料からなる感熱記録材料に前者と同様に支持体側から熱印加し、熱印加したパターン状に昇華染料を昇華させ被記録シートに転写させて画像を得る方法（昇華熱転写）である。電子写真方式は帯電した光導電層に光パターンを与えて静電潜像を形成し、トナー現像後に被記録シートに転写し、熱でトナーを溶融定着する方法が主流である。

【0005】 一方、次のような用途では、透明シートを使用する必要があり、多くは表面に色材受容（吸収）層を設けた透明フィルムを用いて上記のようにして画像形成し記録シートを作成する。例えば、会議等でスライドに代わり使用される機会が増えている OHP フィルム、印刷ポスターや表示板の代わりに使用される機会が増えているバックライトディスプレイ用フィルム、及び第二原図用フィルム等を挙げることができる。

【0006】 これらの記録方式で画像形成された透明フィルムは、得られる画像の色相、彩度、明度に加えて、色材が被記録シートの表面に強固に接着していることが必要であり、さらにインクジェット記録の場合では、精細な画像を得る上で液状インクを早く吸収し、インクニジミやインク溜まりの無いことが要求される。これらの問題点を解決する為に、従来から様々な提案がなされている。例えば、インクジェット記録の場合、特開昭 55-146786 号公報には上記色材吸収層に吸水性ポリマーの使用、特開昭 56-80489 号公報には溶解性又は膨潤性物質の使用が提案され、また多数のポリマー系（ポリビニルアルコール（PVA）、ポリビニルピロリドン（PVP）、ポリエチレンオキサイド（PEO）、カルボキシメチルセルロース（CMC））が提案されている。しかしながら、これらはポリマーの親水性基あるいは解離性基による水性インクの浸透効果を利用したものであり、膜を厚くした場合でも十分なインク吸収速度が得られず、また混色染みの抑制が不充分であった。

【0007】 また色材受容層を多孔質膜にすることにより毛細管現象でインク吸収させる方法が、特公昭 63-22997 号公報、特公昭 63-56876 号公報、特公平 3-21357 号公報、特公平 3-48867 号公報、特開昭 57-14091 号公報、特開昭 60-61286 号公報、特開昭 60-214989 号公報、特開昭 61-22983 号公報及び特開昭 62-227684 号公報に提案されている。これらはインク吸収性については比較的高いものであるが、本発明者の検討によると多孔質膜の孔径が大き過ぎるため光が散乱（回折散乱、ミー散乱）されて光学的透明性が低いことから、光

の透過性が要求される用途には適さない。

【0008】さらに色材受容層に多孔質無機顔料を用いる方法が、特開昭55-144172号公報、特開昭56-148584号公報、特開昭56-148585号公報、特開昭62-273881号公報、特公平3-24906号公報及び特開昭60-245588号公報等に提案されている。これらも、本発明者の検討によると、顔料の粒径が大き過ぎるため光散乱が起こり、十分な光透過性を示すとは言えない。また特定の屈折率の無機微粒子を用いる方法が、特公昭61-53958号公報、特公昭61-60793号公報に、さらに屈折率が約1.45である各種のシリカ粒子を用いる方法が、特開昭55-51583号公報（非膠質シリカの使用）、特開昭56-148583号公報（微粉ケイ酸の使用）、特開昭61-19389号公報（コロイダルシリカの使用）に提案されている。また一次粒子径10～30nmの気相法シリカを二次凝集させて使用する方法が特公平3-56552号公報に提案されている。しかしながら、このような屈折率又は粒子径のみ規定された多孔質無機顔料を使用した色材受容層では、十分な透明性が得られないことが明らかとなった。

【0009】一方、擬ペーマイト系微粒子を用いて微細な空孔を有する色材受容層が形成された記録シートが、特開平2-276670号公報及び特開平3-281383号公報に記載されている。これらは、本発明者の検討によると、インク吸収性については良好であるが、屈折率が約1.65と高い為、十分な透明性が得られない事が明らかとなった。

【0010】

【発明が解決しようとする課題】本発明者は、特に上記インク吸収性と透明性に優れた記録シートを得るために種々検討を重ねてきた。そして、シリカの超微粒子を用い、且つこれを分散させるための結合剤の量を極めて低減させた状態で高度に分散させることにより形成される色材受容層を透明支持体上に設けることにより達成されることが明らかとなった。また、このようにシリカの超微粒子を高度に分散させることにより得られる色材受容層は、極めて小さい細孔からなる空隙を高い空隙率で有する三次元網目構造を有していることが判明した。このような三次元網目構造により、上記インク吸収性と透明性の両立を可能にしたものである。

【0011】従って、本発明はインク記録、熱転写記録又は電子写真記録により透明な画像シートを得ることができる色材受容層を有する記録用シートを提供することを目的とする。また、本発明は、透明性が高く、得られた画像の色相、彩度及び明度に優れた記録用シートを提供することを目的とする。更に、本発明は、液状インクを迅速に吸収し、インクニジミやインク溜まりの無い精細な画像を得ることができるインク記録に適した透明性の高い記録用シートを提供することを目的とする。また

本発明は、熱転写記録においては色材が被記録シートの表面に強固に接着し、また電子写真記録においてはトナー密着性と耐エンボス性に優れた透明性の高い記録用シートを提供することを目的とする。

【0012】

【課題を解決するための手段】上記目的は、透明支持体上に、透明な色材受容層が設けられてなる記録用シートにおいて、色材受容層が、空隙率50～80%を有する三次元網目構造の層であり、そしてその三次元網目構造が、平均1次粒子径が10nm以下のシリカ微粒子と水溶性樹脂とから形成されており、且つシリカ微粒子と水溶性樹脂の重量比が1.5:1～10:1の範囲にあることを特徴とする記録用シートにより達成することができる。

【0013】上記本発明の記録用シートの好ましい態様は下記のとおりである。

- 1) 三次元網目構造の空隙を形成する細孔が、5～30nmの平均直径（平均細孔径）を有する上記記録用シート。
- 2) 三次元網目構造の空隙を形成する細孔が、0.5～0.9ml/gの細孔容量を有する上記記録用シート。
- 3) シリカ微粒子が、無水珪酸である上記記録用シート。
- 4) シリカ微粒子が、表面に1nm²当たり2～3個のシラノール基を有する上記記録用シート。
- 5) 三次元網目構造が、シリカ微粒子が凝集した10～100nmの粒径を有する二次粒子の連結により形成される鎖からなる上記記録用シート。
- 6) 水溶性樹脂が、ポリビニルアルコールである上記記録用シート。
- 7) 色材受容層が、100～250m²/gの比表面積を有する上記記録用シート。
- 8) 色材受容層が、70%以上の光線透過率を有する上記記録用シート。
- 9) 色材受容層の層厚が、10～50μmであるインクジェット記録用の上記記録用シート。
- 10) 色材受容層の層厚が、0.1～10μmである電子写真用又は感熱記録用上記記録用シート。

【0014】前述のように、従来からインク記録に於けるインク吸収機構として、水性インクの場合は親水性基や解離性極性基を有する吸水性ポリマーを色材受容層に設ける方法と、色材受容層を多孔質構造とする方法がある。毛細管現象による多孔質構造の方がインク吸収性が高く及び混色滲みが少ない点で優れているが、多孔質であるため光散乱により光透過性が減少することから、透過型で使用するOHPフィルム、バックライトディスプレイ及び第二原図用フィルムには適さない。この光透過性を向上させて、しかも空隙率の高い構造とする為には、1.5前後の屈折率を有する極めて小さい粒径の超微粒子である本発明の特定のシリカを少量の結合剤樹脂

とともに分散液中に分散し、塗布乾燥することで、この超微粒子の二次粒子からなる三次元網目構造が形成された色材受容層を透明支持体上に設けることができ、これにより達成できる。

【0015】すなわち、本発明の記録用シートは、透明支持体と、支持体上に形成された透明な色材受容層とからなる基本構成を有する。本発明の色材受容層は、空隙率50～80%を有する三次元網目構造の層であり、そして三次元網目構造は、平均1次粒子径が10nm以下のシリカ微粒子と水溶性樹脂を、シリカ微粒子と水溶性樹脂の重量比が1.5:1～10:1の範囲で用いて形成することにより得ることができる。

【0016】本発明の色材受容層を形成するシリカの粒子構造（三次元網目構造）を表わす模式図を、図1に示す。また、その色材受容層表面のシリカの粒子構造の走査型電子顕微鏡写真を図2に、そして断面のシリカの粒子構造の走査型電子顕微鏡写真を図3に示す。図1には、表面を水溶性樹脂2で被覆されたシリカ微粒子が凝集した二次粒子1が、空隙を構成する細孔3を形成しながら互いに連結して形成された三次元網目構造が示されている。また、図2及び図3は、色材受容層の表面及び断面に見られるシリカの粒子構造を10万倍の倍率で走査型電子顕微鏡を通して撮影された写真である。図1の模式図とほぼ対応した三次元網目構造が、色材受容層の表面にも、内部にも存在することが分かる。

【0017】二次粒子1を形成するシリカ微粒子は、平均一次粒子径が10nm以下（好ましくは3～10nm）で且つ屈折率が1.45であり、そしてこのシリカ微粒子を用いて、上記範囲の量にて水溶性樹脂を用いて分散させることにより、微粒子の二次粒子を鎖単位とする3次元ネットワーク構造が形成され、このネットワークの間隙に微細孔が形成されることから、空隙率が極めて高く光透過性の多孔質膜構造が得られる。一般に、粒子径が小さくなるに従い、重量当たりの表面積（比表面積）が大きくなり表面特性による粒子相互作用の影響が強くなる。この為分散液中に超微粒子を高度に分散したゾル液においては、分散液中で粒子同士が衝突した場合、表面の電気特性や水素結合により粒子同士が付着する確率が高くなり、つまり粒子同士の接触点の少ない、いわゆるフロキュレーション（軟凝集状態）が生じ、更にこれが連結した三次元ネットワーク構造となりウエットゲルが生じる。これを乾燥し分散液が蒸発すると、三次元ネットワーク（網状）構造内に微細な空隙が生じ、多孔質キセロゲルが生成する。これは広義に解釈すればゾルゲル法と言われる方式の応用であり、本発明の色材受容層の形成もこれを利用したものである。この三次元網状構造内に微細な空隙の形成は、粒子が小さくなる程顕著であり、本発明のように特に平均一次粒子径が10nm以下のシリカ微粒子を（及び上記範囲内の量にて水溶性樹脂と組み合わせる）を用いた場合に光散乱の少な

い細孔径30nm以下で且つ空隙率が高い透明多孔質膜を形成することができる。

【0018】シリカ粒子は、表面のシラノール基による水素結合により粒子同士が付着やすい為、上記のように平均一次粒子径が10nm以下（好ましくは3～10nm）の場合に於いて空隙率の大きい構造を形成することができる。シリカ粒子は製造法により湿式法と乾式法に大別される。湿式法はケイ酸塩の酸分解により活性シリカを生成し、これを適度に重合させ凝集沈降させ含水シリカを得る方法が主流である。一方の乾式法シリカは、ハロゲン化珪素の高温気相加水分解による方法（火炎加水分解法）、ケイ砂とコークスを電気炉中でアークにより加熱還元酸化し、これを空気で酸化する方法（アーク法）で無水シリカを得る方法が主流である。これらの含水シリカ及び無水シリカは表面のシラノール基の密度、空孔の有無等の相違があり異なった性質を示すが、無水珪酸（無水シリカ）の場合に特に空隙率が高い三次元構造を形成し易く好ましい。この理由は明確ではないが表面のシラノール基の密度が含水シリカの場合は5～8個/nm²と多く粒子が密に凝集（アグリゲート）し易く、一方の無水シリカの場合は2～3個/nm²と少ない為、粗な軟凝集（フロキュレート）となり空隙率が高い構造になると推定される。

【0019】上記三次元網目構造は、シリカ微粒子が凝集した10～100nmの粒径を有する二次粒子の連結により形成されることが好ましく、さらに20～50nmが好ましい。また三次元網目構造の50～80%の空隙率は56～80%であることが好ましく、その空隙を形成する細孔は、5～30nmの平均直径（平均細孔径）を有することが好ましく、特に10～20nmが好ましい。細孔の容量（細孔容量）は、0.5～0.9ml/gが好ましく、更に0.6～0.9ml/gが好ましい。更に、色材受容層の比表面積は、100～250m²/gの範囲が好ましく、特に120～200m²/gが好ましい。また色材受容層の光線透過率は、70%以上が好ましい。

【0020】シリカ微粒子以外に、本発明の目的を損なわない範囲で、次の材料を用いても良い。使用される微粒子としては、透明性を低下させない点から屈折率が1.40～1.60にあるものが好ましく、例えばコロイダルシリカ、珪酸カルシウム、ゼオライト、カオリナイト、ハロイサイト、白雲母、タルク、炭酸カルシウム、硫酸カルシウム等を挙げることができる。

【0021】本発明では、色材受容層（膜）である三次元構の形成を容易にし、その膜強度を高める為、及び乾燥時の膜のヒビ割れを防止する為に、シリカ微粒子と共に結合剤として水溶性樹脂が使用される。このシリカ微粒子と水溶性樹脂の比率（P/B比：水溶性樹脂の重量1に対するシリカ微粒子の重量）は膜構造にも大きな影響を与える。P/B比が大きくなると空隙率、細孔容積、表

面積（単位重量当たり）が大きくなる。10を超えた場合は、膜強度、乾燥時のヒビ割れに対する効果が無く、1.5未満では空隙が樹脂で塞がれ空隙率が減少してインク吸収性能が低下する。この為、PB比は1.5～10の範囲が好適である。特にOHPフィルムのように手で直接触る場合は充分な膜強度を得る必要があり、PB比は5以下が特に好ましく、またインクジェットプリンターで高速インク吸収性を得る為にはPB比は2以上が特に好ましく、従ってPB比は2～5の範囲がさらに好適である。

【0022】例えば、上述のような平均一次粒子径が10nm以下の無水シリカと水溶性樹脂をPB比が2～5で水溶液中に完全に分散し塗布乾燥した場合、シリカ粒子の二次粒子を鎖単位とする三次元網目構造が形成され、平均細孔が30nm以下、空隙率が50%以上、細孔比容積0.5ml/g以上、比表面積が100m²/g以上の透光性の多孔質膜（色材受容層）を容易に形成することができる。

【0023】水溶性樹脂の例としては、親水性構造単位としてヒドロキシル基を有する樹脂として、ポリビニルアルコール（PVA）、セルロース系樹脂（メチルセルロース（MC）、エチルセルロース（EC）、ヒドロキシエチルセルロース（HEC）、カルボキシメチルセルロース（CMC）等）、キチン類及びデンプン；エーテル結合を有する樹脂としてポリエチレンオキシド（PEO）、ポリプロピレンオキシド（PPO）、ポリエチレングリコール（PEG）及びポリビニルエーテル（PVE）を；そしてアミド基またはアミド結合を有する樹脂としてポリアクリルアミド（PAAM）およびポリビニルピロリドン（PVP）を挙げることができる。また、解離性基としてカルボキシル基を有するポリアクリル酸塩、マレイン酸樹脂、アルギン酸塩及びゼラチン類を；スルホン基を有するポリスチレンスルホン酸塩、アミノ基、イミノ基、第3アミン及び第4アンモニウム塩を有するポリアリルアミン（PAA）、ポリエチレンイミン（PEI）、エポキシ化ポリアミド（EPAm）、ポリビニルピリジン及びゼラチン類を挙げることができる。透明性の観点からシリカ微粒子に組み合わせる樹脂の種類が重要であり、無水シリカの場合は、PVA特に、低鹼化度（好ましくは鹼化度70～90%）PVAが光透過性の点で好適である。PVAは、構造単位に水酸基を有するが、この水酸基とシリカ粒子表面のシラノール基が水素結合を形成して、シリカ粒子の二次粒子を鎖単位とする三次元網目構造を形成し易くすると考えられる。これにより、空隙率の高い構造の色材受容層が得られると考えられる。このようにして得た色材受容層はインクジェット記録において、毛細管現象によって急速にインクを吸収し且つインクニジミやインク溜まりの無い精細な記録が可能であるばかりでなく、感熱記録における色材、そして電子写真記録におけるトナーを強

固に接着できる。この理由は、色材やトナーが多孔質層の細孔内にもぐり込み、その結果として三次元網目構造に起因する形状的なアンカー効果により色材等を強固に固定する為である。また、無機微粒子の割合が多い為、耐熱性が高く電子写真記録に於ける耐エンボス性も高い特徴がある。

【0024】色材受容層の層厚は、インクジェット記録の場合は液滴を全て吸収するだけの吸収容量をもつ必要がある。例えばインク量が8nl/mm²の場合で、空隙率が60%であれば約15μm以上の膜が必要となる。インクジェット記録の場合の場合は、10～50μmの範囲が好ましい。感熱転写や電子写真方式の場合は色材あるいはトナーを表面に吸着することから、薄膜で十分であり、0.1～10μmが好ましい。

【0025】この色材受容層を、主として構成するシリカ微粒子と水溶性樹脂は、それぞれ単一素材でも良いし複数の素材の混合系でもよい。また色材受容層は主としてシリカ微粒子と水溶性樹脂からなるがそれ以外に粒子の分散性を高める為に各種の無機塩類、PH調整剤として酸アルカリを含んでいてもよい。また塗布適性や表面品質を高める目的で各種の界面活性剤を使用してもよい。表面の摩擦帯電や剥離帯電を抑制する為、あるいは電子写真法に於いて表面電気抵抗を調整する為にイオン導電性を持つ界面活性剤や電子導電性を持つ金属酸化物微粒子を含んでいてもよい。またインク記録に於いて色素を固定し耐水性を高める目的で媒染剤を使用してもよい。また表面の摩擦特性を低減する目的で各種のマット剤を含んでいてもよい。また色材の劣化を抑制する目的で各種の酸化防止剤、紫外線吸収剤を含んでいてもよい。

【0026】また色材受容層と透明支持体の間に接着性を高めたり、電気抵抗を調整する等の目的で下塗層を設けてもよい。さらに色材受容層は、透明支持体の片面に設けても良いし、またカー等を抑する為に、両面に設けても良い。また、色材受容層を片面のみに設ける場合は、その反対面に光透過性を高めるために、反射防止膜を設けても良い。この反射防止膜の屈折率（ n_r ）は、透明支持体の屈折率が n_s の場合は $n_s^{1/2}$ に近く、そしてその膜厚は $\lambda/4n$ に近いことが好ましい（但し、 λ は使用するOHPランプの波長である）。

【0027】上記透明支持体として使用できるフィルムは透明でOHPあるいはバックライトディスプレイで使用される時の輻射熱に耐える性質を有する材料であれば用いることができる。その材料としては、ポリエチレンフタレート等のポリエステル類；ニトロセルロース、セルロースアセテート、セルロースアセテートブチレート等のセルロースエステル類、さらにポリスルホン、ポリフェニレンオキシド、ポリイミド、ポリカーボネート、ポリアミド等を挙げることができる。これらの中

で、ポリエチレンフタレートが好ましい。フィルムの厚さは、特に制限はないが、50～200 μ mのものが取り扱い易く好ましい。また支持体フィルムはコロナ放電処理、火炎処理、紫外線照射処理を施したものを使用してもよい。

【0028】色材受容層は、例えば下記のようにして透明支持体上に設けることができる。色材受容層形成用塗布液は、平均一次粒子径10nm以下のシリカ微粒子を、水中に添加して（例、10～15重量%）、高速回転湿式コロイドミル（例、クレアミックス（エム・テクニク（株）製））を用いて、例えば10000rpm（好ましくは5000～20000rpm）の高速回転の条件で20分間（好ましくは10～30分間）分散させた後、ポリビニルアルコール水溶液（例、シリカの1/3程度の重量のPVAとなるように）を加えて更に、上記と同じ条件で分散を行ない、ついでpHを4～5に調整することにより得ることができる。このようにして得られた塗布液は、均一ゾルであり、これを下記の塗布方法により、透明支持体上に形成することにより、本発明の三次元網目構造を有する色材受容層を得ることができる。即ち、上記均一ゾルの塗布液を支持体上に塗布した後乾燥することにより、溶媒である水を蒸発させる。この蒸発により塗布膜がゲル化濃度に達した時点でウェットゲルが形成され、更に乾燥が進行することにより多孔質キセロゲルが形成され、本発明の色材受容層を得ることができる。

- ①乾式シリカ微粒子（平均1次粒子径：7nm； 10重量部
屈折率：1.45；表面シラノール基：2～3/nm²；
エアロジルA300（日本エアロジル（株）製））
- ②ポリビニルアルコール（鹸化度88%；重合度3500； 3.3重量部
PVA235（クラレ（株）製））
- ③イオン交換水 136.0重量部

①のシリカ微粒子を、③のイオン交換水（73.3重量部）中に添加して、高速回転湿式コロイドミル（クレアミックス（エム・テクニク（株）製））を用いて、10000rpmの条件で20分間分散させた後、ポリビニルアルコール水溶液（イオン交換水の残り62.7重量部に溶解させたもの）を加えて更に、更に上記と同じ条件で分散を行ない、ついでpHを4～5に調整して色材受容層形成用塗布液を得た。

【0032】（2）塗布乾燥

この塗布液を100 μ mの厚みの二軸延伸したポリエチレンテレフタレート表面をコロナ放電処理し、その表面にエアナイフコーターを用いて塗布し、熱風乾燥機により70℃（風速5m/秒）で1分間乾燥した後、更に150℃で10分間乾燥した。これにより乾燥膜厚が30 μ mの色材受容層を形成した。これにより、インクジェット用の記録用シートを得た。得られた色材受容層の表面及び断面の走査型電子顕微鏡写真（100000倍）を、それぞれ図2及び図3に示す。これらの写真よ

【0029】上記色材受容層の形成は、例えば、上記塗布液に所望によりさらに帯電防止剤等を加えて得られた塗布液を上記透明フィルム上に塗布、加熱乾燥することにより実施することができる。塗布は、例えばエアードクターコーター、ブレードコーター、ロッドコーター、ナイフコーター、スクイズコーター、リバースロールコーター、パーコーター等の公知の塗布方法で行なうことができる。乾燥は、熱風乾燥機により比較的低温で（好ましくは、50～90℃（風速3～8m/秒））で0.5～3分間乾燥した後、更に比較的高温（好ましくは、120～180℃で5～20分間）で乾燥することが、特に膜厚が厚い時の色材受容層の乾燥時のフレ防止の点から好ましい。また、塗布、乾燥後、例えばスーパーカレンダー、グロスカレンダー等で加熱、加圧下にロールニップ間を通すことにより、表面平滑性、透明性及び塗膜強度を向上させることが可能である。しかしながら、このような処理は空隙率を低下させるため（即ちインク吸収性が低下するため）、空隙率の低下が少ない条件を設定して行なう必要がある。

【0030】

【実施例】

【0031】【実施例1】

（1）色材受容層形成用塗布液の組成（以下の全ての塗布液の配合量を示す重量部の値は、全て固形分又は不揮発分を表わす）

り、得られた色材受容層は三次元網目構造を有することが分かる。

【0033】【比較例1】実施例1において、平均1次粒子径7nmの乾式シリカ粒子の代わりに平均1次粒子径30nmの乾式シリカ粒子（屈折率1.45；MOX-80（日本エアロジル（株）製）を使用した以外は実施例1と同様にしてインクジェット用の記録用シートを作製した。

【0034】【比較例2】実施例1において、平均1次粒子径7nmの乾式シリカ粒子の代わりに平均1次粒子径13nmのアルミナ粒子（屈折率1.75；Aluminum Oxide C（日本エアロジル（株）製）を使用した以外は実施例1と同様にしてインクジェット用の記録用シートを作製した。

【0035】【比較例3】実施例1において、色材受容層形成用塗布液の組成を下記の組成に変更した以外は実施例1と同様にしてインクジェット用の記録用シートを作製した。

- ①乾式シリカ微粒子（平均1次粒子径：7 nm； 6.65重量部
屈折率：1.45；表面シラノール基：2～3個/nm²；
エアロジルA300（日本エアロジル（株）製））
②ポリビニルアルコール（鹸化度88%；重合度3500；6.65重量部
PVA235（クラレ（株）製））
③イオン交換水 86.7重量部

【0036】上記で得られたインクジェット用の記録用シートについて、以下の測定方法によってそのインクジェット適性を評価した。

（1）インク吸収速度

インクジェットプリンター（PIXEL JET；キャノン（株）製）により、記録用シートへの赤、黄、青及び黒のベタ印字直後（約10秒後）に紙を接触押圧し、インクの紙への転写の有無で下記のように判定した。

AA：紙にインキが転写されなかった。

CC：紙にインキが転写された。

（2）インク混色しみ

上記と同一のプリンターを用いて、記録用シートに印刷された赤、黄、青及び黒の各々のベタ印字部境界におけるしみ出し程度によって判定した。

AA：しみ出しがなかった。

BB：しみ出しが少し認められた。

CC：しみ出しがかなり認められた。

（3）ドット径

上記と同一のプリンターを用いて、黒インクの記録用シートに印刷されたドットの直径を顕微鏡で測定した。

（4）色濃度

上記と同一のプリンターを用いて、記録用シートに印刷された赤、黄、青及び黒のベタ印字部を、光学濃度計（X-Rite 310TR；X-Rite社製）で測定した。上記評価の結果を下記の表1に示す。

【0037】

【表1】

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表1

	インク 吸収 速度	インク 混色 しみ	ドット 直径 (μ m)	色 濃 度			
				黄	青	赤	黒
実施例1	AA	AA	101	1.50	1.28	1.48	1.69
比較例1	AA	AA	108	1.42	1.21	1.40	1.66
比較例2	AA	AA	107	1.46	1.26	1.41	1.67
比較例3	CC	BB	122	1.38	1.11	1.40	1.59

【0038】上記で得られたインクジェット用の記録用シートについて、以下の測定方法によってその物理特性を評価した。

（5）平行光線透過率

ヘイズメーター（HGM-2DP；スガ試験機（株）製）を用い平行光線透過率を測定した。

（6）平均細孔径、（7）空隙率、（8）細孔比容積及び（9）比表面積は水銀ポロシメータ（ポアサイザー9

320-PC2；島津製作所（株）製）を用いて測定し、それぞれの分布を得て、平均値を計算した。

（10）シリカ粒子の二次粒径

得られた色材受容層を走査型電子顕微鏡で観察することにより求めた。上記評価の結果を下記の表2に示す。

【0039】

【表2】

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表2

	透過率 (%)	細孔径 (nm)	空隙率 (% (V/V))	細孔比容積 (ml/g)	比表面積 (m ² /g)	二次粒径 (nm)
実施例1	81.3	15	61	0.77	162	40
比較例1	62.0	35	43	0.45	83	140
比較例2	40.2	21	51	0.52	103	110
比較例3	68.3	12	32	0.38	114	40

【0040】〔実施例2〕

(1) 色材受容層形成用塗布液の組成 (以下の全ての塗

布液の配合量を示す重量部の値は、全て固形分又は不揮発分を表わす)

①乾式シリカ微粒子 (平均1次粒子径: 7 nm; 1重量部

屈折率: 1.45; 表面シラノール基: 2~3/nm²;

エアロジルA300 (日本エアロジル (株) 製))

②ポリビニルアルコール (鹸化度88%; 重合度3500 0.33重量部

PVA235 (クラレ (株) 製))

③イオン交換水

147.97重量部

①のシリカ微粒子を、③のイオン交換水 (82.3重量部の大部分) 中に添加して、高速回転湿式コロイドミル (クレアミックス (エム・テクニク (株) 製)) を用いて、10000rpmの条件で20分間分散させた後、ポリビニルアルコール水溶液 (イオン交換水の残り65.67重量部に溶解したもの) を加えて更に、更に上記と同じ条件で分散を行ない、ついでpHを4~5に調整して色材受容層形成用塗布液を得た。

【0041】(2) 塗布乾燥

この塗布液を100μmの厚みの二軸延伸したポリエチレンテレフタレート表面をコロナ放電処理し、その表面に#12パーエアーナイフコーターを用いて塗布し、熱風乾燥機により100℃で10分間乾燥した。これにより乾燥膜厚が0.5μmの色材受容層を形成した。これにより、電子写真用の記録用シートを得た。得られた色材受容層を走査型電子顕微鏡 (100000倍) で観察したところ、色材受容層は三次元網目構造を有することが認められた。

【0042】〔比較例4〕実施例1において、平均1次粒子径7nmの乾式シリカ粒子の代わりに平均1次粒子

径30nmの乾式シリカ粒子 (屈折率1.45; MOX-80 (日本エアロジル (株) 製)) を使用した以外は実施例1と同様にして電子写真用の記録用シートを作製した。

【0043】〔比較例5〕実施例1において、平均1次粒子径7nmの乾式シリカ粒子の代わりに平均1次粒子径13nmのアルミナ粒子 (屈折率1.75; Aluminum Oxide C (日本エアロジル (株) 製)) を使用した以外は実施例1と同様にして電子写真用の記録用シートを作製した。

【0044】このようにして得られた電子写真用の記録用フィルムを下記の方法によりその特性を評価した。

11) トナー密着性

電子写真複写機 (VIVACE-120; 富士ゼロックス (株) 製) で複写し、得られた複写フィルムについて全面が画像の部分 (黒ベタ部分) をセロテープ剥離試験し、セロテープ剥離前後のトナー画像の光学濃度を光学濃度計 (X-Rite 310TR、X-Rite社製) にて測定し、下式によりトナー密着性を評価した。

セロテープ剥離後の光学濃度

× 100 (%)

セロテープ剥離前の光学濃度

【0045】12) 耐エンボス性

上記と同一の電子写真複写機で画像を複写し、得られた複写フィルムについて目視でフィルムの凹凸ムラ (凹凸が大きくなると平滑性の低下をもたらす) 有無を観察し、耐エンボス性を下記のように評価した。

AA: 複写フィルムに凹凸ムラが無かった。

CC: 複写フィルムに凹凸ムラがあり、平滑性が低下していた。

上記と同一の電子写真複写機で画像を複写し、得られた複写フィルムの黒ベタ部分の光学濃度を光学濃度計 (X-Rite 310TR、X-Rite社製) にて測定した。また、前記(5)~(10)の物理特性についても測定した。上記測定結果 ((5)~(10) 及び (11)~(13)) を下記の表3に示す。

【0047】

【表3】

表3

	接着性 (%)	耐エン ボス性	転写 濃度	透過率 (%)	細孔径 (nm)	空隙率 (% (V/V))	細孔 比容積 (ml/g)	比表 面積 (m ² /g)	二次 粒径 (nm)
実施例2	83	AA	1.14	87	15	60	0.77	162	40
比較例4	69	AA	1.11	82	35	43	0.45	83	140

比較例 5 73 AA 1.12 87 21 51 0.52 103 110

【0048】

【発明の効果】本発明の記録用シートは、インク記録においては液状インクを早く吸収しインク滲みやインク溜まりの無い精細な画像が得られ、また熱転写記録においては色材が被記録シートの表面に強固に接着し、また電子写真記録においてはトナー密着性と耐エンボス性に優れた透明記録用シートである。本発明の記録用シートは、高い透明性が得られ易い1.5に近い屈折率を有し、散乱強度が小さい極めて小さい粒径の超微粒子の特定のシリカを少量の結合剤樹脂とともに分散液中に高度に分散し、塗布乾燥することで、この超微粒子の二次粒子からなる微小な細孔を有する三次元網目構造が形成された色材受容層が透明支持体上に設けられたものである。従って、この色材受容層は、微小な細孔を有する三次元網目構造の層であり、且つ高い空隙率を有している。即ち、1.5に近い屈折率のシリカ粒子の二次粒子の連結で形成された三次元網目構造により微小な細孔が

形成されているので、光散乱が少なく高い透明性を示す。また高い空隙率により、インクの吸収性、滲み防止、そして熱転写記録や電子写真記録においては色材あるいはトナーの接着性が向上する。上記理由から、本発明の記録用シートは種々の記録方法に適した透明な記録用シートであるといえることができる。

【図面の簡単な説明】

10 【図1】本発明の色材受容層を形成するシリカの粒子構造の一例を示す模式図である。

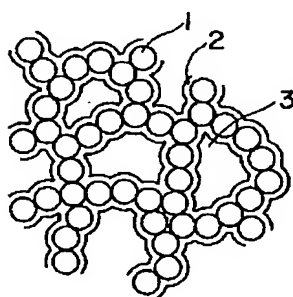
【図2】本発明の色材受容層の表面を形成するシリカの粒子構造の一例の走査型電子顕微鏡写真である。

【図3】本発明の色材受容層の断面を形成するシリカの粒子構造の一例の走査型電子顕微鏡写真である。

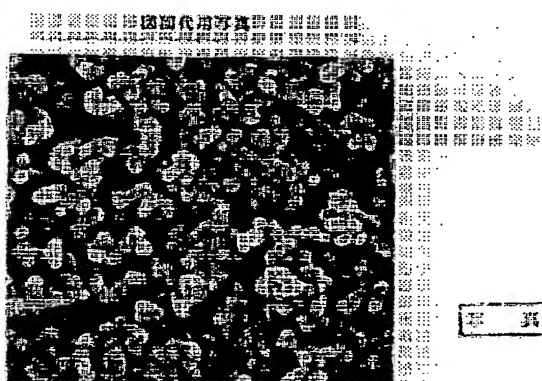
【符号の説明】

- 1 シリカ微粒子が凝集した二次粒子
- 2 水溶性樹脂
- 3 細孔

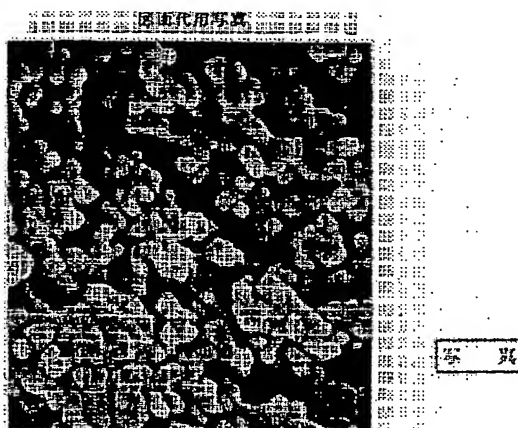
【図1】



【図2】



【図3】



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